

Environmental Effects of Dredging Technical Notes



Lower Limits of Organic Carbon Normalization: Results of Fish/Sediment/Water Equilibrium Partitioning Studies

Purpose

This technical note reports the initial results of studies measuring biota/sediment/water equilibrium partitioning of a polychlorinated biphenyl (PCB) congener. The focus of this technical note is on the validity of normalizing concentrations of neutral organic chemicals on sediment total organic carbon (TOC) when sediment TOC concentrations are low.

Background

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Over the past 10 years, the U.S. Environmental Protection Agency (EPA) has aggressively pursued development of single-chemical sediment quality criteria (SQC). Equilibrium partitioning of neutral organic chemicals between the organic carbon fraction of bedded sediments and the interstitial water of the sediments provides the theoretical basis for the most popular approach to development of SQC. The solution phase of the chemical in equilibrium with the sediment is considered to represent the bioavailable fraction and to enable the conversion of existing water quality criteria (WQC) into SQC or sediment quality standards.

In this approach, sediment total organic carbon is considered to be the primary sediment phase accounting for sorption of neutral organic chemicals, and concentrations of these chemicals are therefore normalized to the TOC fraction. A chemical-unique partition coefficient (K_{oc}), applied to the TOC-normalized

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chemical concentration, is used to estimate the solution-phase concentration for calculation of the bioavailable fraction, which is then compared with WQC. Criteria documents for the pesticides endrin and dieldrin, and for several polynuclear aromatic hydrocarbons, have been released by the EPA for public review and may soon be promulgated.

State water quality standards are pass/fail criteria, as are Federal WQC for ocean disposal of dredged material. EPA has not made clear the intended purpose of SQC relative to regulation of dredging activities but has stated an intention to recommend them as water quality standards to be used by the States as applicable relevant additional requirements. Under that scenario, SQC will be applied to dredging regulation as pass/fail criteria.

The promulgation of SQCs with the intent that they be used as standards will result in confounding of effects-based testing procedures as they are now practiced in dredged sediment regulation under the Ocean Dumping Act and the Clean Water Act (Wright, Engler, and Miller 1992; Wright and Wilson 1995). Under such circumstances, it is imperative that the quality of the SQC estimations and the degree of uncertainty surrounding them be clearly understood.

The Corps of Engineers has not been directly involved in the development of SQC. For that reason Work Unit 32571, "Relationship Between Sediment Geochemistry and Biological Impacts," was initiated under the Long-term Effects of Dredging Operations Program to investigate the validity of SQC for the regulation of sediments. The research reported in this technical note continues that effort.

Additional Information

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Introduction

SQC predictions are dependent on the linearity of bioavailability of sediment-contaminating chemicals (that is, interstitial water concentrations) with sediment TOC content. However, several researchers have found in previous investigations that the freely dissolved fraction of several nonpolar organic chemicals is not consistently predictable from the TOC content of the sediment (Brannon and others 1993, 1995a, 1995b). The source, aromaticity, intraparticle sorption processes, and the structure and composition of humic materials have all been reported to affect the partitioning of neutral organic chemicals between sediments and water (Gauthier, Seitz, and Grant 1987; Brusseau and Rao 1989;

Grathwohl 1990). The suggested lower limit for the validity of organic carbon normalization stated in the technical documentation supporting SQC is 0.2 percent (DiToro and others 1991). This lower limit was derived by separate adsorption and desorption experiments in which the partition coefficients of several organic chemicals were normalized to the organic carbon content of sediments, and greatest departure from linearity was observed to occur at about 0.2 percent TOC in the sediments.

Sorption experiments conducted without the presence of living organisms can provide valuable information regarding the physicochemical behavior of chemicals in sediment/water systems, but do not truly address questions of bioavailability. For that reason, an exposure system (Figure 1) was designed to allow modeling of the distribution of an introduced chemical among the principal partitioning compartments represented by fish, water, and sediment (McFarland and others 1992, 1994). The partitioning data are fitted using a three-compartment closed kinetic model (Figure 2) (Gibaldi and Perrier 1982) and the simultaneous equations (Equations 1-3) describing intercompartmental distribution of the chemical as a function of time.

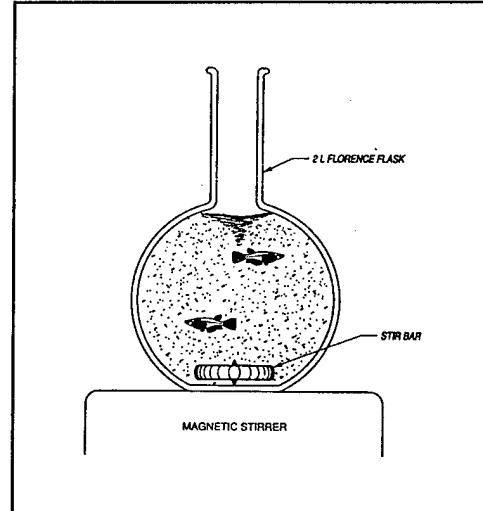


Figure 1. Exposure system

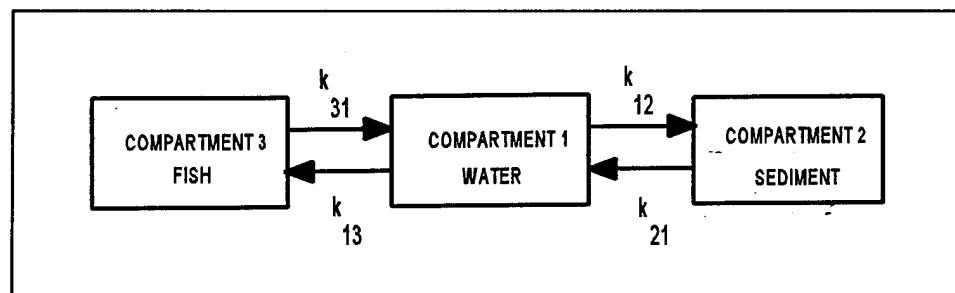


Figure 2. Three-compartment closed kinetic model

$$dX_w/dt = k_{21}X_s + k_{31}X_f - k_{12}X_w - k_{13}X_w \quad (1)$$

$$dX_s/dt = k_{12}X_w - k_{21}X_s \quad (2)$$

$$dX_f/dt = k_{13}X_w - k_{31}X_f \quad (3)$$

In this model X_w , X_f , and X_s are the mass of PCB-52 (micrograms as total radioactivity) in water, fish, and sediment, respectively, and k_{12} , k_{21} , k_{13} , and k_{31} are the intercompartmental transfer coefficients describing rates of mass transfer among the compartments. Complete derivations are given in Feldhaus,* as are solutions for the hybrid coefficients used to project mass distribution at equilibrium. This model and exposure system can be used to test the lower limit of TOC normalization for predicting bioavailability as described below.

Bioaccumulation factors (BAF) are calculated as the non-normalized ratios of the transfer coefficients:

$$BAF = (k_{13}/k_{31})/(k_{12}/k_{21}) \cdot 0.4 \quad (4)$$

For neutral organic chemicals that partition passively, BAFs can be expected to vary inversely with sediment organic carbon content when other factors are held constant. In fact, the assumption of linearity of bioavailability with sediment TOC requires that this relationship be constant down to the lower limit of validity of TOC normalization. Biota/sediment accumulation factors (BSAFs) are calculated similarly, but normalized to lipid content (fl) in the fish and organic carbon content (foc) in the sediment:

$$BSAF = [(k_{13}/k_{31})/fl]/[(k_{12}/k_{21})/foc] \cdot 0.4 \quad (5)$$

The factor 0.4 in Equations 4 and 5 is necessary to correct for mass differences (Landrum 1983). The relationships derive from the facts that equilibrium partitioning of a chemical between an organic and an aqueous phase is described by the ratio of the forward and reverse rate constants (Kubinyi 1978) and that water is the common phase for partitioning to both sediment and organism (McFarland and others 1994). Whereas BAF is in theory linear and inversely proportional to sediment TOC (all else being constant), BSAF is a simple factorial difference in concentration or mass of chemical in organism lipids and sediment TOC. These relationships can be used to test the linearity of bioavailability of a neutral organic chemical with sediment TOC as follows:

1. If the lower limit of validity of organic carbon normalization is, in fact, 0.2 percent, then BAFs should regress linearly with TOC to that limit and BSAFs for all sediments above that level should be constant.
2. If the limit is a higher or a lower percentage of organic carbon, then that should be revealed by the TOC concentration at which a break in the linearity of BAFs occurs and above which BSAFs are constant and below which they differ.

* Jane Feldhaus. "A toxicokinetic compartmental model for the determination and prediction of a biota-sediment accumulation factor for PCB-52," Ph.D. dissertation (in preparation), Northeast Louisiana University, Monroe, LA.

3. If factors other than TOC contribute significantly to the total activity of the sediment compartment, this should be reflected by nonlinear BAFs and nonconstant BSAFs.

Materials and Methods

Freshwater sediments were collected from various locations throughout the country, air-dried, finely ground using a mortar and pestle, and analyzed for total organic carbon. TOC values were measured using a Shimadzu 5050 TOC analyzer equipped with a model SSM-5000 Solids Module. The five sediments selected for study were subsampled and analyzed for particle size distribution by sieving and for bulk mineralogy by X-ray diffraction analysis. The sediment with the highest TOC content was also subsampled and heated in a muffle furnace for 12 hr at 450 °C to drive off the carbon, thus providing a sediment with 0 percent TOC.

Stock cultures of Japanese medaka (*Oryzias latipes*) were obtained from Gulf Coast Research Laboratory, Ocean Springs, MS, and from Aquatic Research Organisms, Hampton, NY, or were cultured in the laboratory at the Waterways Experiment Station. The male medaka were maintained separately in a Living Stream on a diet of flake fish food at a temperature of 20 ± 2 °C and a photoperiod of 16 hr light:8 hr dark. Only males were used as experimental organisms in order to achieve greatest uniformity in weight and lipid content.

The experimental setup consisted of a series of 2-L florence flasks placed on individual stir plates (Figure 1). Four hundred milligrams of air-dried sediment, sieved to ≤ 500 µm, was placed in each flask, along with 2 L of charcoal-filtered aged tap water, two adult male Japanese medaka, and a Teflon-coated stir bar. The stir plates were turned on, and 100 µL [^{14}C]-PCB-52 (4.26 µg/mL in methanol, specific activity = 0.202 µCi/µg, obtained from Sigma Chemical Company, St. Louis, MO) was added to each flask, yielding an aqueous exposure concentration of 0.213 µg/L. In the initial experiment, a sample schedule of 0, 1, 2, 4, 12, 36, 72, 96, and 120 hr of exposure was used. Subsequently, the 72- and 96-hr exposures were deleted when it appeared that their inclusion was unnecessary for curve-fitting. At each sample time the flasks were taken down, and the water, sediment, and fish were extracted and analyzed for total radioactivity. Six replicate flasks were used for each time point.

A portion of the exposure water was centrifuged, and a 100-mL aliquot was extracted in a separatory funnel with 25 mL 4:1 hexane:acetone and then re-extracted with 20 mL hexane. The extracts were combined, concentrated under nitrogen to about 2 mL, and transferred to a scintillation vial. Liquid scintillation cocktail (15 mL of Packard Ultima Gold, Packard Instrument Company, Meriden, CT) was added, and the samples were counted on a Packard 2500 Tri-Carb liquid scintillation counter using a quenched calibration curve.

Upon removal from the exposure flasks, the fish were sacrificed and the intestinal tracts were removed from the fish. The fish were homogenized with

20 mL of acetone using a Brinkmann Polytron homogenizer, and the homogenates were centrifuged to collect the acetone extracts. The extraction was repeated and the extracts were combined. Two milliliters of water and 10 mL of hexane were then added for partitioning of the acetone extract between hexane and water. The hexane layers were collected and split. One aliquot was air-dried in a tared container for gravimetric determination of lipid content, and the other aliquot was concentrated under nitrogen for PCB-52 analysis as described above. The intestinal tracts were solubilized using Solvable tissue solubilizer (Dupont NEW, Boston, MA) and were analyzed for PCB-52.

The sediment from each exposure flask was collected by centrifugation and was extracted three times using 10 mL of acetone, with 20 min of sonication (Branson 2200 ultrasonic bath) each time. The acetone extracts were combined, concentrated under nitrogen, and analyzed for PCB-52 as above.

Results and Discussion

The five treatments are identified in the tables and figures by an alphanumeric code in which the letters designate the source of the sediment and the numeric suffix designates the percentage of TOC in the sediment. Mineral composition and percentage dry weight TOC of the five sediments are shown in Table 1. Sediment MSL-0.0 was a subsample of sediment SL-2.03 heated to destroy the organic carbon before use. Heating also changed the mineral composition, destroying the clay components. The sediments were all predominantly fine quartz sand. Smectite, an expandable clay mineral, constituted approximately 25 percent, by dry weight, of FP-0.331 and SL-2.03, and about 9 percent of BL-0.963. Smectite was not an identifiable component of the other sediments. Expandable clays tend to covary with sediment TOC content and have been shown to influence sorption of PCBs to a far greater extent than nonswelling clays (Uzgiris and others 1995). It was considered that their presence could influence bioavailability at low TOC concentrations. However, it is well recognized that organic carbon predominantly accounts for the sorption behavior of neutral chemicals on soils and sediments.

The data as masses of PCB-52 in each compartment of the system (0.4 g sediment, 2 L water, 1.0 g fish) at each sampling time were fitted to the model using the Gauss-Newton algorithm and PCNONLIN (Metzler and Weiner 1992). The model generally fit the data well in all treatments, with most of the variability being contributed by the sediment compartment. The fitted nonlinear regressions and means of the measured masses of PCB-52 in each compartment at each sampling interval are shown in Figure 3. The curves illustrate a typical pattern in which there is a rapid initial decline of PCB-52 in the water and a concomitant rapid uptake by the sediment, which then begins to decline in less than 24 hr. Uptake by the fish is slower, due most likely to the rate-limiting effect of gill blood flow (Karara and McFarland 1992). Partitioning of PCB-52 to all three compartments approaches an asymptote by 120 hr.

Table 1. Sediment Identification Code and Composition

Composition	Sediments				
	MSL-0.0	NY-0.103	FP-0.331	BL-0.963	SL-2.03
TOC (%)	0.0	0.103	0.33	0.96	2.03
Quartz	Major	Major	Major	Major	Major
Na feldspar	NF ¹	Major	Minor	Minor	Minor
K feldspar	Minor	Major	Trace	Minor	Minor
Calcite	NF	Minor	Trace	Minor	Trace
Dolomite	NF	Minor	Trace	Major	Trace
Kaolinite	NF	NF	Trace	Trace	Trace
Mica	NF	Trace	Trace	Trace	Trace
Chlorite	NF	Trace	NF	NF	NF
Smectite	NF	NF	Major	Minor	Major

¹ Not found.

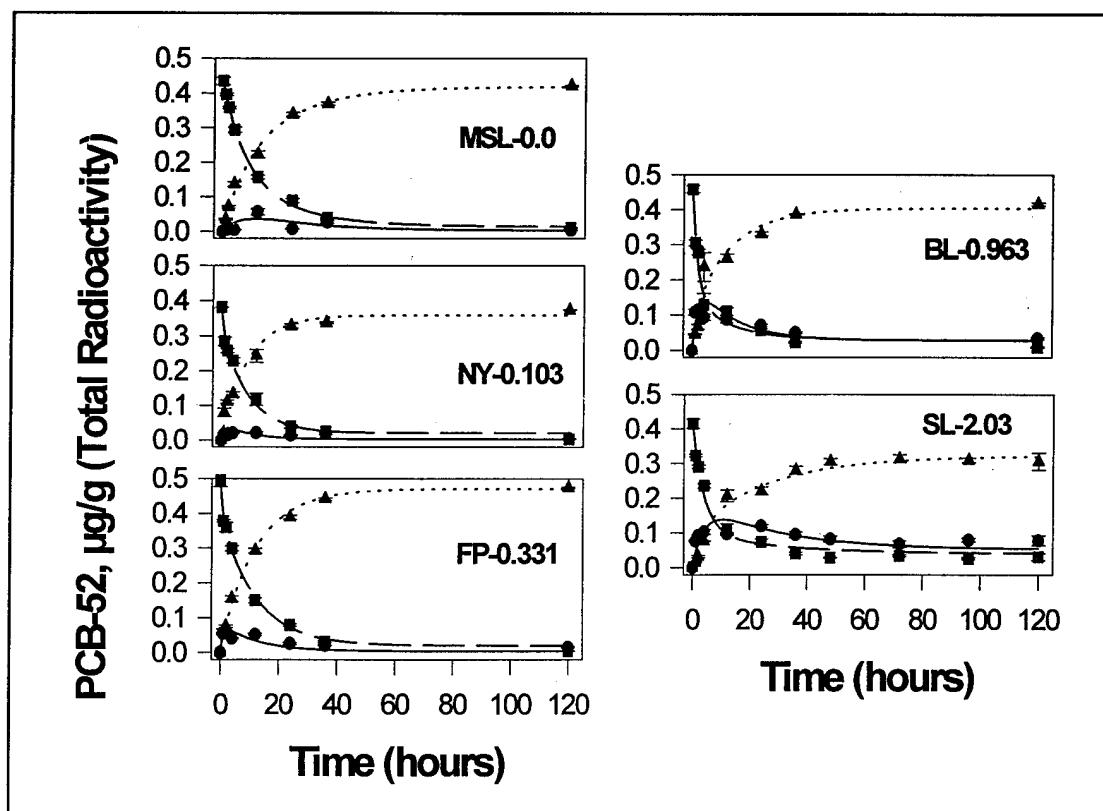


Figure 3. Mass distribution of PCB-52 over time in the five treatments. Symbols with horizontal lines are measured values (error bars). Lines are model-predicted regressions on the measured data (■, water; ●, sediment; ▲, fish)

BAFs were calculated using Equation 4 and the intercompartmental transfer coefficients for each replicate of each treatment. BSAFs were similarly calculated using Equation 5 for the four treatments having measurable organic carbon on the sediments. The grand mean (0.043415, standard error = 0.017688, N = 210) of all lipid fraction (fl) measurements was used in all BSAF calculations, and the organic carbon fraction (foc) was the TOC appropriate to the treatment, expressed as the decimal fraction.

Linearity of bioavailability with sediment organic carbon content was tested by Lack of Fit analysis on the four treatments having measurable organic carbon (Figure 4). The BAFs for each replicate of each of the four treatments were regressed on sediment TOC, and the result was a significant lack of fit ($P \leq 0.05$). The relationship between TOC content and mean BAFs and the constancy of BSAFs were assessed by statistical comparisons among the sediments using analysis of variance followed by Tukey's Honestly Significant Difference test (SAS Institute, Inc. 1988) (Table 2). Because of violations of normality or equality of variances assumptions, the BAFs and BSAFs were converted to normalized ranks (rankits) prior to analysis with Tukey's test. The BAFs fell in two groups. The lower group included the two treatments having 0.963 and 2.03 percent sediment TOC. The higher group included the three treatments with zero to 0.331 percent TOC, and these were not statistically distinguishable. The difference between the two groups was about an order of magnitude and shows clearly the influence of sediment organic carbon on the partitioning behavior of PCB-52 between sediments and fish. This result is also shown in Figure 5.

Table 2 and Figure 5 show a different grouping for the BSAFs. As expected, the two highest TOC sediments were statistically indistinguishable, confirming the validity of normalization of PCB-52 on sediment organic content in the range of 1 percent and above. However, the mean BSAF for the sediment having 0.103 percent TOC was also statistically similar to the two high-TOC treatments, while that of the 0.331 percent TOC treatment was higher and statistically different from the rest. This anomalous result was not explained by the presence or absence of swelling clays in the sediments.

It was concluded from these results that bioavailability of PCB-52 is highly variable and not linear with sediment organic carbon content at low TOC levels. It appears that the lower limit of validity of organic carbon normalization may be higher than the 0.2 percent cited in the technical document supporting equilibrium partitioning SQCs (DiToro and others 1991). Examination of Figures 4 and 5 shows what appears to be an inflection or a break point in the relationship in the region below 0.963 percent and above 0.331 percent TOC.

Clearly, more work is needed to fully understand these results. Equilibrium partitioning experiments involving additional sediments, sediment mineralogy, sediment TOC polarity, other variables, and other chemicals are ongoing or planned. It is recommended that, until definitive characterization of the phenomenon has been completed, normalization of neutral chemical concentrations on sediment TOC at levels less than 1 percent should be used cautiously in

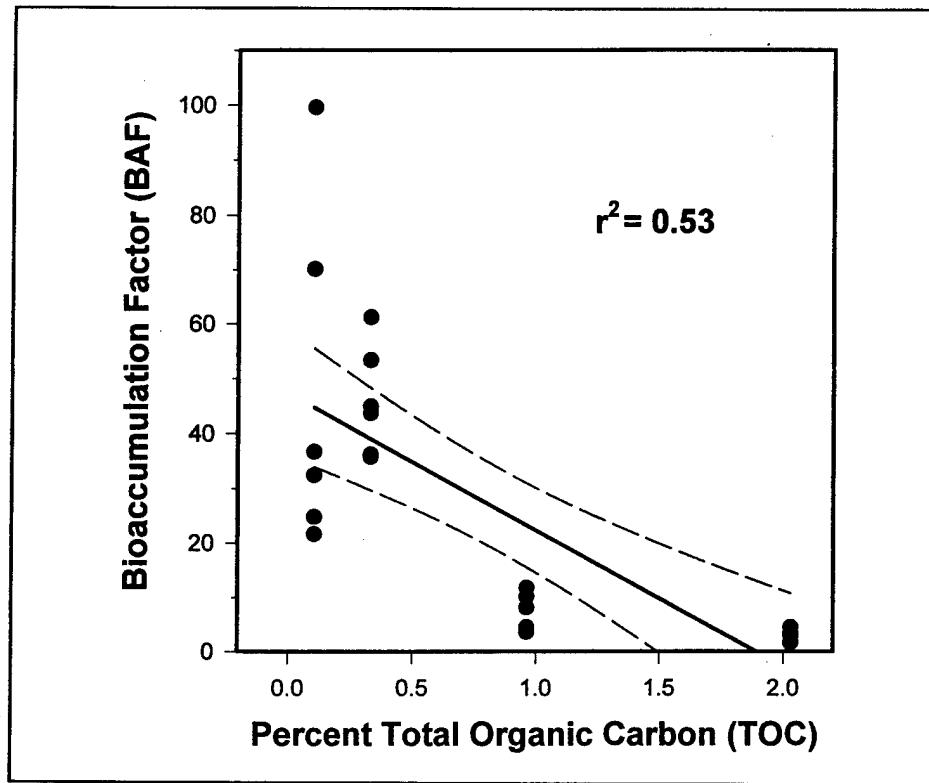


Figure 4. Linear regression and 95-percent confidence interval on bioaccumulation factors calculated for each replicate ($n = 6$) of the four treatments having organic carbon. (Lack of fit analysis: $DF = 2$, $F = 4.00882$, $P = 0.034355$)

Table 2. Fish/Sediment Ratios (BAF) and Biota/Sediment Accumulation Factors (BSAF) with Analysis of Variance Results, Means, Standard Errors (SE), and Mean Comparisons (Tukey Group)

Treatment	BAF		BSAF	
	$F = 16.84$	$P = 0.0001$	$F = 14.56$	$P = 0.0001$
	$N = 30$	$R^2 = 0.729$	$N = 24$	$R^2 = 0.686$
Treatment	Mean (SE)	Tukey Group ¹	Mean (SE)	Tukey Group
MSL-0.0 ²	62.81 (12.66)	A	NA ³ (NA)	NA
NY-0.103	47.55 (12.58)	A	1.128 (0.298)	A
FP-0.331	45.88 (4.053)	A	3.498 (0.309)	B
BL-0.963	7.144 (1.394)	B	1.585 (0.309)	A
SL-2.03	2.925 (0.445)	B	1.368 (0.208)	A

¹ Within a group, means with the same letter designation do not differ significantly ($P_{\alpha/2} \leq 0.025$).

² Numeric suffix denotes percent TOC.

³ Not applicable.

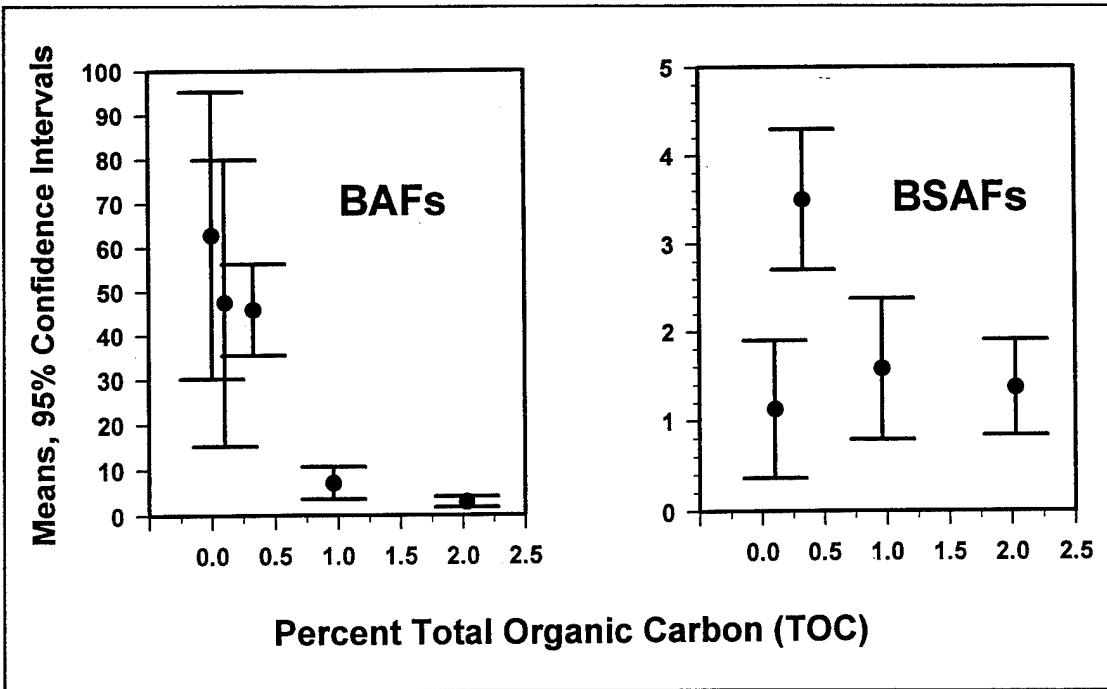


Figure 5. Bioaccumulation factor (BAF) and biota/sediment accumulation factor (BSAF) means (●) and 95-percent confidence intervals (vertical bars and caps) as a function of treatment percent TOC

estimating bioavailability and should not be used in criteria-based regulatory decision-making.

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